



(19) Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 618 286 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 93105232.8

(51) Int. Cl.⁵: **C11D 3/22, C11D 3/20,
C11D 3/00**

(22) Date of filing: **30.03.93**

(43) Date of publication of application:
05.10.94 Bulletin 94/40

(84) Designated Contracting States:
**AT BE CH DE DK ES FR GB GR IE IT LI LU NL
PT SE**

(71) Applicant: **AUSIMONT S.p.A.**

**31, Foro Buonaparte
I-20100 Milano (IT)**

Applicant: **CERESTAR HOLDING BV**
Nijverheidsstraat 1
P.O. Box 9
NL-4550 AA Sas Van Gent (NL)

(72) Inventor: **Burzio, Fulvio**
Via Francesco Ferruccio 6
I-20145 Milano (IT)
Inventor: **Beck, Roland**
13/3 Ave Gossiaux
B-1160 Brussels (BE)

(74) Representative: **Sama, Daniele et al**
Sama Patents
Via Masera, 10
I-20129 Milano (IT)

(54) **Process for decreasing the build up of inorganic incrustations on textiles and detergent composition used in such process.**

(57) A process for decreasing the build-up of inorganic incrustations on textiles deriving from water hardness and due to repeated washing cycles with detergent compositions comprises the addition to the washing bath of a non-reducing carbohydrate and/or non-reducing carbohydrate derivative as co-builder.

EP 0 618 286 A1

The present invention relates to a process for decreasing the build-up of inorganic incrustations on fabrics deriving from water hardness and due to repeated washing cycles with detergent compositions.

More particularly, the present invention relates to a process for decreasing the build-up of inorganic incrustations wherein a co-builder is added to the washing cycle, and to detergent and/or antiincrustating composition containing said co-builder.

It is well known that detergents contain builders in order to support detergent action and to eliminate calcium and magnesium ions (hardness ions), which arise partly from the water and sometimes also from soil and fabrics.

In case of multiple washing cycles the washing performance significantly reduces because of the build up of inorganic incrustations on fabrics and on washing machine components. Such build up of inorganic incrustations on fabrics decreases the flexibility of fibres and consequently shorten the fabric life, in addition to greying the tissue.

A well known builder is the sodium tripolyphosphate which has excellent properties in the washing process even at low concentrations. Despite its many advantageous properties, it causes serious ecological problems, namely eutrophication of standing or slowly flowing surface waters leading to extreme algal growth which adversely influences marine organisms. Therefore, the use of phosphate free detergents is of great importance.

Some substitutes of phosphate builders such as zeolites have been adopted. However, zeolites alone in water softening have poor efficiency. Therefore, good antiincrustating effects are achieved only in the presence of auxiliary compounds called co-builders.

The most widely used co-builders are synthetic polymers and/or co-polymers of olefinic mono-or dicarboxylic acids such as acrylic and maleic acid and copolymers of said monomers with other allylic or vinylic monomers. The common characteristic of these polymeric materials is their minimal biodegradability which leads to ecological problems.

There are known other non-polymeric co-builders, such as EDTA (ethylenediaminetetraacetic acid sodium salt), NTA (nitrilotriacetic acid sodium salt) and phosphonates. Like the polymeric co-builders these substances too are non-biodegradable.

It is therefore an object of the present invention to provide a process for decreasing the build-up of inorganic incrustations on fabrics and on washing machine components by using co-builders which are very efficient in reducing incrustation build up during washing cycles and which are cheap and biodegradable.

Another object of the present invention is to provide detergent and/or antiincrustating compositions containing said biodegradable co-builders.

It has surprisingly been found that carbohydrates and carbohydrate derivatives (carbohydrate derived polyols) show a high efficiency in reducing incrustation build up when combined with detergents, particularly with zeolite-based detergents.

In accordance with one aspect of the present invention, there is provided a process for decreasing the build-up of inorganic incrustations on fabrics and on washing machine components during multiple washing cycles with detergent compositions characterized by the addition to the washing cycle of a co-builder based on non-reducing carbohydrates and/or non-reducing carbohydrate derivatives.

The co-builders based on non-reducing carbohydrates and the non-reducing carbohydrate derivatives can be incorporated into the detergent compositions or added as such directly to the washing bath.

The co-builders used according to the present invention are preferably non-reducing di-, tri- or oligo-saccharides and/or hydrogenated mono-, di- or oligo-saccharides.

Representative examples of non-reducing carbohydrates include sucrose, trehalose, kestoses, raffinose, stachyose, verbascose, nystose, inulin, and mixtures thereof.

Representative examples of non-reducing carbohydrate derivatives include glycerol, erythritol, threitol, xylitol, arabitol, ribitol, sorbitol, mannitol, galactitol, tallitol, allitol, altritol, iditol, gulitol, heptitols, anhydrohexitols, maltitol, lactitol, maltotritol, palatin, alkyl glucosides, alkyl-polyglucosides, hydrogenated leucrose, hydrogenated glucose syrup, hydrogenated maltose syrup, hydrogenated invert sugar, hydrogenated high fructose syrups, and mixtures thereof.

The cobuilders are preferably the so-called sugar alcohols, particularly sugar alcohols having the general formula $\text{HOCH}_2(\text{CHOH})_n\text{CH}_2\text{OH}$ where n has a value from 2 to 5 inclusive. Particularly preferred are the hexitols specially sorbitol or mannitol. Mixtures of sugar alcohols may also be used e.g. mixtures of sorbitol and mannitol and mixtures known as hydrogenated starch hydrolysates which contain sorbitol, maltitol, maltotriitol and higher oligomers.

The co-builders preferably are hexitols, such as sorbitol and/or mannitol; or sucrose and/or glycerol.

In accordance with another aspect of the present invention, there are provided detergent and/or antiincrustating compositions containing the hereinbefore defined co-builders. These compositions may also

contain usual components such as anionic, non-ionic, cationic or amphoteric surfactants, alkali metal salts (e.g. sodium carbonate, sodium silicate), neutral salts (e.g. sodium sulphate), zeolite, bleaching agents, bleaching activators and minor ingredients.

In accordance with one preferred embodiment of the present invention the co-builders are used in combination with zeolite-based detergents.

The co-builders used according to the present invention are particularly efficacious in the presence of inorganic persalts, such as sodium perborate tetrahydrate or monohydrate.

The amount of the co-builders used in the process can vary from 1 g/washing cycle to 40 g/washing cycle, and preferably from 2 g/washing cycle to 20 g/washing cycle. This amount is comprised within the range of from 0,5% to 20% and preferably comprised within the range of from 1% to 10%, expressed as 100% dry substance of the detergent or antiincrustating compositions.

The co-builders used according to the present invention are naturally derived, biodegradable compounds. In combination with detergents they reduce the build up of inorganic incrustations on fabrics and on washing machine components. Such activity is more significant at high temperatures e.g. at 90 °C.

The present invention is disclosed in still further detail in the following examples, which are supplied for purely illustrative and not limiting purposes.

EXAMPLE 1

The anti-incrustation test was carried out running 25 cycles in automatic machines under the following conditions:

- washing program at 60 °C,
- linen load: 3 kg cotton ballast (white and clean)/washing cycle,
- dosage of detergent composition without co-builder: 192 g/washing cycle,
- water hardness: 45 °F (Ca:Mg = 3:1).

As test fabric for incrustation build-up detection a white, non optically brightened cotton sheet of 50 cm x 50 cm was used. The sheet was previously desized and had the following characteristics: weight = 180 g/m², warp = 24 yarns, weft = 24 yarns.

Three commercial washing machines of Italian market of CANDY, ARISTON and S. GIORGIO were used in the antiincrustation test.

The test fabric was consecutively washed in these washing machines by changing the washing machine after every 5th washing cycle, to avoid systematic errors.

At the end of the 25th washing cycle a 10 cm x 50 cm strip was cut off from the test fabric, dried in an oven at 60 °C for 4 hours and weighed.

Then it was burnt and calcined at 900 °C in a muffle. The residue after calcination, expressed as % of the strip weight, represented the % of inorganic incrustation.

The detergent composition (without co-builder) used for the test and assumed as a reference, was the following:

40	<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 70%;">- surfactants (anionic + non-ionic + soap)</td><td style="width: 30%; text-align: right;">14%</td></tr> <tr> <td>- zeolite 4A</td><td style="text-align: right;">27%</td></tr> <tr> <td>- sodium silicate</td><td style="text-align: right;">3%</td></tr> <tr> <td>- sodium carbonate</td><td style="text-align: right;">10%</td></tr> <tr> <td>- sodium perborate tetrahydrate</td><td style="text-align: right;">20%</td></tr> <tr> <td>- sodium sulphate</td><td style="text-align: right;">26%</td></tr> </table>	- surfactants (anionic + non-ionic + soap)	14%	- zeolite 4A	27%	- sodium silicate	3%	- sodium carbonate	10%	- sodium perborate tetrahydrate	20%	- sodium sulphate	26%
- surfactants (anionic + non-ionic + soap)	14%												
- zeolite 4A	27%												
- sodium silicate	3%												
- sodium carbonate	10%												
- sodium perborate tetrahydrate	20%												
- sodium sulphate	26%												
45													

As co-builder sorbitol was used at the level of 6 g/washing cycle.

The inorganic incrustation build up determined after the 25th washing cycle is set forth in Table 1.

For comparative purposes the same test was repeated at 60 °C and at 90 °C with the difference that no co-builder was added to the washing cycles. The results obtained are reported in Table 1.

EXAMPLE 2

Example 1 was repeated with the difference that the washing cycles were carried out at 90 °C.

The inorganic incrustation build up determined after the 25th washing cycle is reported in Table 1.

The test results of Examples 1 and 2 show that the use of sorbitol in the washing reduces the build up of inorganic incrustation on the fabric and this reduction is more significant at 90 °C.

EXAMPLE 3

Example 1 was repeated with the difference that sorbitol was replaced by mannitol and it was used in an amount of 2 g/washing cycle.

5 The determined inorganic incrustation build up is reported in Table 1.

EXAMPLE 4

Example 3 was repeated with the difference that the washing cycles were carried out at 90 °C.

10 The determined inorganic incrustation build up is reported in Table 1.

EXAMPLE 5

Example 4 was repeated with the difference that the mannitol amount was 8 g/washing cycle.

15 The obtained results set forth in Table 1 show that the increase in the amount of mannitol contributes to a more significant decrease in the inorganic incrustation build up.

EXAMPLE 6

20 Example 5 was repeated with the difference that mannitol was substituted by an equal amount of sucrose.

The determined inorganic incrustation build up is reported in Table 1.

EXAMPLE 7

25 Example 5 was repeated with the difference that mannitol was substituted by an equal amount of glycerol.

The values obtained for inorganic incrustation build up and reported in Table 1 demonstrate that the co-builders based on carbohydrates and carbohydrate derivatives show excellent antiincrustating properties in 30 combination with detergents.

TABLE 1

Co-builder	Dosage g/wash	Incrustation in %	
		60 °C	90 °C
absent (reference)	-	1,9	3,9
Sorbitol (Examples 1 and 2)	6	1,1	1,8
Mannitol (Examples 3 and 4)	2	1,5	1,4
Mannitol (Example 5)	8	-	0,86
Sucrose (Example 6)	8	-	1,1
Glycerine (Example 7)	8	-	1,3

Claims

50 1. A process for decreasing the build up of inorganic incrustations on fabrics and on washing machine components during multiple washing cycles characterized by the addition to the washing cycle of a co-builder based on non-reducing carbohydrates and/or non-reducing carbohydrate derivatives.

55 2. The process according to Claim 1, characterized in that the non-reducing carbohydrate derivatives are hydrogenated mono-, di- or oligo-saccharides and/or non-reducing di-, tri- or oligo-saccharides.

3. The process according to Claim 1, characterized in that the co-builder as such is added directly to the washing bath.
4. The process according to Claim 3, characterized in that the co-builder is added in amount ranging from 5 1 g/washing cycle to 40 g/washing cycle, preferably from 2 g/washing cycle to 20 g/washing cycle.
5. The process according to Claim 1, characterized in that the co-builder is incorporated in the detergent composition.
10. 6. Detergent and/or antiincrustating composition containing co-builder based on non-reducing carbohydrates and/or non-reducing carbohydrate derivatives.
15. 7. Detergent and/or antiincrustating composition according to Claim 6, characterized in that the co-builder is a sugar alcohol having the general formula $\text{HOCH}_2(\text{CHOH})_n\text{CH}_2\text{OH}$ where n has a value from 2 to 5 inclusive
20. 8. Detergent and/or antiincrustating composition according to Claim 6, characterized in that the co-builder is selected from the group consisting of sucrose, trehalose, kestoses, raffinose, stachyose, verbascose, nystose, inulin, alkyl glucosides, alkyl-polyglucosides, glycerol, erythritol, threitol, xylitol, arabinol, ribitol, sorbitol, mannitol, galactitol, tallitol, allitol, altritol, iditol, gulitol, heptitols, anhydrohexitols, maltitol, lactitol, maltotriitol, palatinit, hydrogenated, leucrose, hydrogenated glucose syrup, hydrogenated maltose syrup, hydrogenated invert sugar, hydrogenated high fructose syrups, and mixtures thereof.
25. 9. Detergent and/or antiincrustating composition according to Claim 7, characterized in that the co-builder is sorbitol.
10. 10. Detergent and/or antiincrustating composition according to Claim 7, characterized in that the co-builder is mannitol.
30. 11. Detergent and/or antiincrustating composition according to Claim 8, characterized in that the co-builder is sucrose.
35. 12. Detergent and/or antiincrustating composition according to Claim 7, characterized in that the co-builder is glycerol.
13. Detergent and/or antiincrustating composition according to Claim 6, characterized in that it contains zeolites.
40. 14. Detergent and/or antiincrustating composition according to Claim 6, characterized in that it contains the co-builder in an amount ranging from 0.5% to 20%, preferably from 1% to 10%, expressed as 100% dry substance of the detergent or antiincrustating composition.
15. Detergent and/or antiincrustating composition according to Claim 6, characterized in that it contains an inorganic persalt.

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 10 5232
Page 1

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	GB-A-215 813 (LION CORPORATION) * claims 1,3; examples 3-5,8-11 * ---	6-10, 12-15	C11D3/22 C11D3/20
X	EP-A-0 215 637 (UNILEVER NV) * page 2, line 41 - line 50; claims 1-3,11; examples 1c,2,3,4,6-16 * ---	6,8, 9-11, 13-15	
X	CHEMICAL ABSTRACTS, vol. 107, no. 10, 7 September 1987, Columbus, Ohio, US; abstract no. 79987, 'cationic surfactant granules' page 122 ;column 2 ; * abstract * & JP-A-6 257 500 (LION CORP) ---	6-10, 12-15	
X	CHEMICAL ABSTRACTS, vol. 103, no. 14, July 1985, Columbus, Ohio, US; abstract no. 106643, 'granular detergents' page 100 ;column 1 ; * abstract * & JP-A-6 088 100 (LION CORP) ---	6-10, 12-15	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
X	CHEMICAL ABSTRACTS, vol. 88, no. 6, 6 February 1978, Columbus, Ohio, US; abstract no. 39259, 'cleaning composition' page 81 ;column 1 ; * abstract * & JP-A-52 094 304 (YUKEN KAGAKU KOGYO) ---	6,8,11	C11D
A	CHEMICAL ABSTRACTS, vol. 99, no. 4, 25 July 1983, Columbus, Ohio, US; abstract no. 24452, 'powder or granular detergents' page 110 ;column 1 ; * abstract * & JP-A-57 209 998 (NIPPON OILS AND FATS) ---	1-13	
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		21 JULY 1993	KLIER E.K.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 10 5232
Page 2

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 307 748 (HENKEL) * page 3, line 58 - page 4, line 1; claims 1,4,6,7,12 *	6-13	
	-----		TECHNICAL FIELDS SEARCHED (Int. Cl.5)
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	21 JULY 1993	KLIER E.K.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

THIS PAGE BLANK (USPTO)